

# Variations of Dielectric and Piezoelectric Properties of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}\text{O}_3$ Piezoelectric Single Crystal Wafers

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Variations of dielectric and piezoelectric properties between wafers and within a wafer of lead zinc niobate titanate ( $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}\text{O}_3$  (PZNT 91/9)) piezoelectric single crystals (PSC) have been investigated. Curie temperatures ( $T_c$ ) and dielectric constants ( $\epsilon_{33}^T$ ) showed large variations between wafers and within a wafer. On the other hand, variations of  $T_c$  and  $\epsilon_{33}^T$  within a wafer reduced gradually from the part that includes the nucleation point in the crystal (initial part) to the part of the crystal grown later (end part). The coupling factor ( $kt$ ) had small variations between wafers and within a wafer.

Characteristics variations between wafers may be mainly attributable to variations in composition. Obtaining highly homogeneous PZNT PSC by optimizing the growth process is important for improving characteristics variations. On the other hand, characteristics variations within a wafer may be attributable to not only the variations in composition but also influence of the crystal phases and domain structures. Therefore, the relationship of characteristics variations with the crystal phases and domain structures needs to be investigated in the near future.

Key words: PZNT, single crystal, variation, dielectric property, piezoelectric property

## 1. INTRODUCTION

For next-generation ultrasonic transducers for medical echo, nondestructive testing (NDT) and undersea applications, piezoelectric single crystals (PSC) of complex lead perovskites with the general formula  $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3\text{-PbTiO}_3$  ( $\text{B}_1 = \text{Mg}^{2+}, \text{Zn}^{2+}, \text{Ni}^{2+}, \text{Sc}^{3+}$ , etc.;  $\text{B}_2 = \text{Nb}^{5+}, \text{Ta}^{5+}$ , and/or  $\text{W}^{6+}$ ) have been studied in recent years. [1-3] In particular, an extremely large electromechanical coupling factor of longitudinal mode  $k_{33}=92\%$  and a large piezoelectric constant  $d_{33}=1,500$  pC/N were reported for  $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.91}\text{Ti}_{0.09}]\text{O}_3$  (PZNT 91/9) PSC oriented in the (001) plane by Kuwata et al. in 1982. [3] The above electromechanical coupling factor is larger than  $k_{33}<80\%$  and  $k_{33}'<70\%$  of conventional  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  (PZT) ceramics widely used for applications in piezoelectric devices. The large electromechanical coupling factor ( $k_{33}>90\%$  and  $k_{33}'>80\%$ ) and low acoustic impedance ( $Z_{33}'<25$  Mrays) of PZNT 91/9 make it a promising candidate for realizing array probes of greater sensitivity and broader bandwidth. [4]

The authors have already reported on the growth of large PZNT 91/9 PSC by the conventional flux method and the solution Bridgman method. [5, 6] Subsequently they reported on the fabrication of 3.7MHz phased-array probe using the PZNT 91/9 PSC, its pulse echo characteristics and final imaging quality. [7] Moreover, they have improved the Bridgman method to obtain larger crystal with high reproducibility for mass production.[8]

However, some issues respecting these novel PSC still need to be resolved. H. Luo et al. reported that segregation occurred during the growth of single crystals and its electrical properties vary even in the same crystal-ingot. [9] Therefore, the same issue, that of characteristics variations, exists in PZNT PSC.

The purpose of this paper is to investigate the variations of dielectric and piezoelectric properties,  $T_c$ ,  $\epsilon_{33}^T$ ,  $kt$ , between wafers and within a wafer of PZNT PSC grown by the Bridgman method.

## 2. EXPERIMENTS

### 2.1 Crystal growth

The PZNT 91/9 PSC were prepared using the solution Bridgman method. Details of the growth procedures have been described in previous papers. [6, 8] The flux used was PbO. The 45 mol% PZNT 91/9 pellets and 55 mol% PbO powder were placed in a 50-mm-diameter, 200-mm-long, 0.35-mm-thick Pt crucible. An electric furnace was controlled at 1,180°C to grow the PZNT 91/9 PSC. The Pt crucible was driven down through the heat zone at a speed of 0.3-0.4 mm/h.

### 2.2 Transducer fabrication and measurement

The obtained crystal was sliced along the (001) plane after its orientation was determined by Laue X-ray diffraction patterns. About thirty wafers with thickness of 0.36 mm were obtained. The sliced wafers were

lapped to about 0.26 mm in thickness. Then Ni electrode was formed on the both sides of the wafer. The electroded wafers were cut to 12 mm x 25 mm.

Figure 1 shows the fabrication of the rectangular samples for estimating the characteristics variations in this study. Firstly, three wafers were chosen from the initial part, middle part and end part in the crystal. And then the wafers were cut to twelve rectangular samples (3.7 mm x 6.1 mm) with a dicing saw (DISCO, Model DAD-2H/6T). The wheel thickness and cutting speed were 0.05 mm and 1.0 mm/s, respectively. These rectangular samples were used for the measurement of the dielectric and piezoelectric properties.

Temperature dependence of the dielectric constants before poling was measured using a computer-controlled impedance analyzer (HP4192A). The temperature with a maximum dielectric constant indicates a Curie temperature,  $T_c$ .

Poling was performed by applying electric field of 0.3 kV/mm for 10 minutes at 200°C, and subsequently cooling to 30°C in the same electric field. Dielectric constants after poling,  $\epsilon_{33}^T$ , were measured at room temperature using impedance analyzer (HP4192A). Coupling factors,  $kt$ , were measured by means of the resonance-antiresonance method on the basis of IEEE standards using an impedance mode of a network spectrum analyzer (HP4195A).

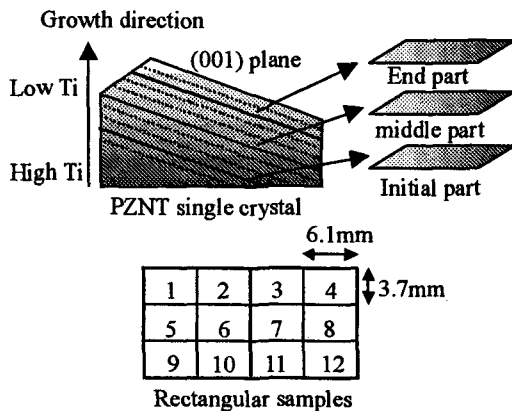


Fig.1 Fabrication of the rectangular samples for estimating the characteristics variations.

### 3. RESULTS AND DISCUSSION

#### 3.1 Obtained crystal

A large PZNT 91/9 PSC, 50 mm in diameter x 30 mm in length was obtained. The weight loss was less than 1.5wt% for the experiment. The crystal growth of PZNT 91/9 PSC occurred mainly at the bottom of the Pt crucible. No serious PbO and/or Pt inclusions were observed in the wafers.

#### 3.2 Variations of dielectric and piezoelectric properties

Table I lists average, maximum and minimum values and their standard deviations of the  $T_c$ ,  $\epsilon_{33}^T$ , and  $kt$ , measured using the rectangular samples fabricated from three wafers of the PZNT 91/9 PSC.

Table I Measured properties of the PZNT 91/9 PSC,  $T_c$ ,  $\epsilon_{33}^T$ ,  $kt$ , using the rectangular samples.

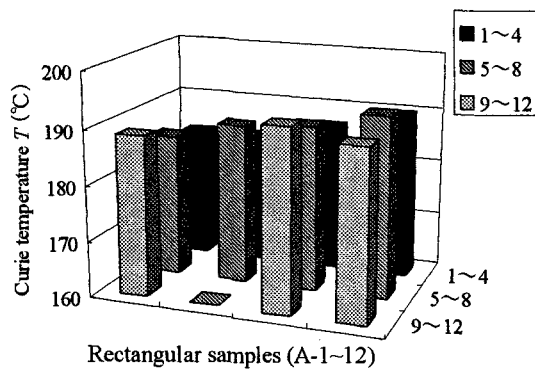
		$T_c$ (°C)	$\epsilon_{33}^T$	$kt$
Initial part (A)	Ave	188	2050	0.567
	$\sigma$	3.1	740	0.010
	Max	193	3240	0.579
	Min	184	1340	0.555
Middle part (B)	Ave	182	2880	0.570
	$\sigma$	1.5	860	0.010
	Max	185	3620	0.588
	Min	181	1450	0.558
End part (C)	Ave	175	3790	0.558
	$\sigma$	0.8	120	0.002
	Max	177	3940	0.559
	Min	174	3600	0.554

Figure 2 shows Curie temperature,  $T_c$ , of rectangular samples fabricated from the three wafers, (a) the initial part, (b) the middle part and (c) the end part of the crystal. The bottom of each three-dimensional figure is in agreement with the sample position illustrated in Fig. 1. In addition, although the great care was exercised in the treatment of samples, some samples were damaged during measurement and the figures lack some data. Average of  $T_c$  was 188°C at the initial part, 182°C at the middle part and 175°C at the end part of the crystal. These results suggest that there is a large variation of  $T_c$  between wafers. The  $T_c$  of the end part is about 10–15°C lower than that of the initial part of the crystal. It is well known that  $T_c$  of  $PbTiO_3$  is 490°C and that of  $Pb(Zn_{1/3}Nb_{2/3})O_3$  is 140°C. Because the PZNT consists of these two materials, high  $T_c$  suggests that  $PbTiO_3$  content is large in the crystal. Therefore, the  $PbTiO_3$  content decreases with distance from the part that includes the nucleation point, and so the  $PbTiO_3$  content at the ending part is smaller than that of the initial part in the crystal.

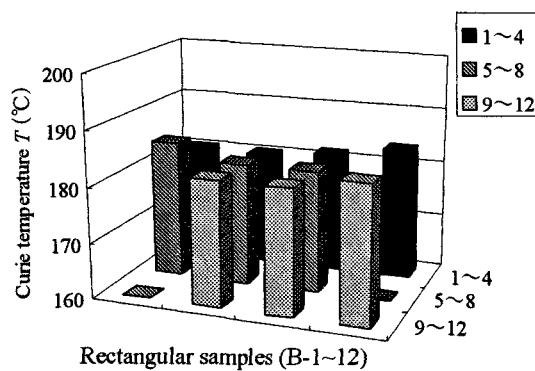
The  $T_c$  varied in the range from 183°C to 190°C at the initial part, which reveals a large variation of  $T_c$  within a wafer. In particular, the  $T_c$  was low at the corner of the wafer in the case of sample A-1, 2, 5, 6; however the  $T_c$  increased gradually to the diagonal corner of the wafer in the case of sample A-7, 8, 11, 12, as shown in Fig. 2(a). On the other hand, the variation of the  $T_c$  within a wafer became smaller from the initial part to the end part; the  $T_c$  varies in the range from 184°C to 193°C at the initial part, from 181°C to 185°C at the middle part and from 174°C to 177°C at the end part.

Figure 3 shows dielectric constants  $\epsilon_{33}^T$  of rectangular samples fabricated from the three wafers, (a) the initial part, (b) the middle part, and (c) the end part of the crystal. In contrast to the  $T_c$ , average of the  $\epsilon_{33}^T$  increased gradually from the initial part to the end part in the crystal; 2,050 at the initial part, 2,880 at the middle part and 3,790 at the end part. The  $\epsilon_{33}^T$  of the end part is about 1,800 higher than that of the initial part of the crystal. These results suggest that there is a large variation of the  $\epsilon_{33}^T$  between wafers. The variation of the  $\epsilon_{33}^T$  within a wafer became smaller from the initial

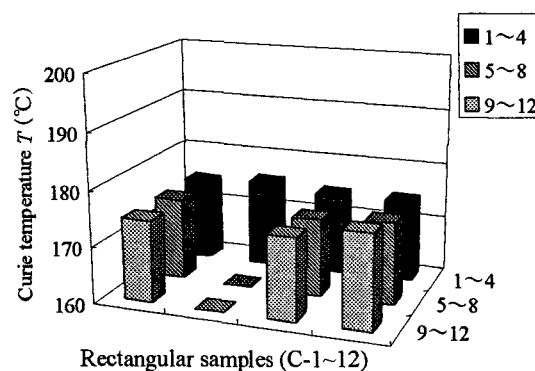
part to the end part, similar to the behavior of the  $T_c$ ; the  $\epsilon_{33}^T$  varied in the range from 1,340 to 3,240 at the initial part, from 1,450 to 3,620 at the middle part and from 3,600 to 3,940 at the end part. However, there were some rectangular samples which showed considerably different  $\epsilon_{33}^T$  although they had almost the same  $T_c$ . In particular, samples B-1, 2, 3, 6, 7 in the middle part had almost the same  $T_c$  of 182°C as shown in Fig. 2(b); however the  $\epsilon_{33}^T$  of their samples varied considerably from 1,450 to 3,320 as shown in Fig. 3(b). The cause of the variation within the wafer may not only be the composition variation because the samples showed almost the same  $T_c$ .



(a) Initial part

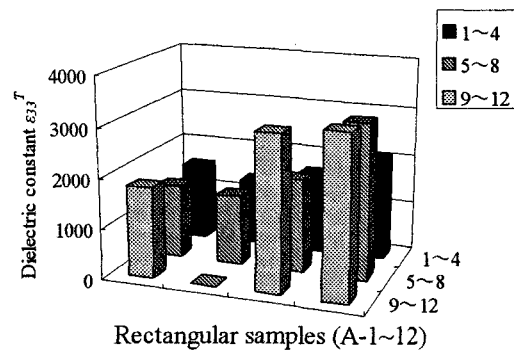


(b) Middle part



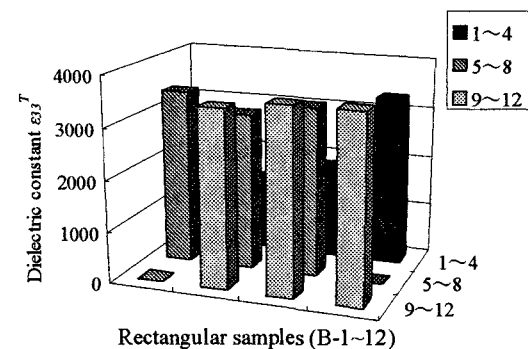
(c) End part

Fig.2 The  $T_c$  of rectangular samples fabricated from the three wafers of the PZNT 91/9.



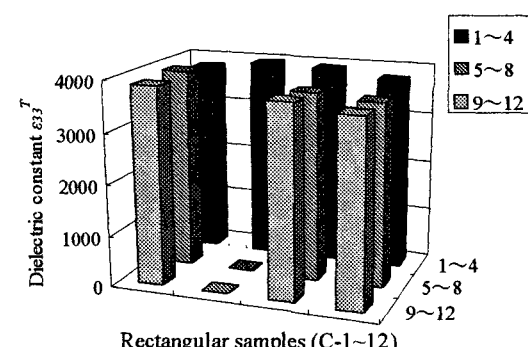
Rectangular samples (A-1~12)

(a) Initial part



Rectangular samples (B-1~12)

(b) Middle part



Rectangular samples (C-1~12)

(c) End part

Fig.3 The  $\epsilon_{33}^T$  of rectangular samples fabricated from the three wafers of the PZNT 91/9.

Coupling factors,  $kt$ , were also measured using the rectangular samples fabricated from the three wafers, the initial part, the middle part and the end part of the crystal. Average of the  $kt$  was 0.567 at the initial part, 0.555 at the middle part and 0.558 at the ending part of the crystal. The variations of the  $kt$  between wafers were small. Moreover, the variations within a wafer were also small in all the parts of the crystal.

Curie temperatures,  $T_c$ , and dielectric constants,  $\epsilon_{33}^T$ , showed large variations between wafers and within a wafer. Figure 1 also illustrates the obtained crystal and the way of cutting (001) wafers from the PZNT PSC. The  $\text{PbTiO}_3$  content decreases with distance from the

part that includes the nucleation point in the PZNT PSC. Authors consider that this composition variation may be the main cause of the characteristics variations. The growth direction of the PZNT PSC is not constant because a seed crystal is not used for the growth. As a result, the growth direction mostly leans slightly from the (001) direction as shown in Fig. 1. The (001) wafers should be cut parallel to the (001) plane, which is different from the growth direction. Therefore, every wafer consists of parts grown at different time, and Ti composition varies gradually within the wafer. This composition variation must be the cause of the characteristics variations within a wafer as well as between wafers.

On the other hand, the characteristics variations within a wafer were less at the end part. The cause is considered to be that the end part has low Ti composition and mainly consists of rhombohedral phase, which is different from the MPB composition of the PZNT 91/9 with rhombohedral and tetragonal phases. The dielectric and piezoelectric properties of those phases differ from each other, because they have different directions and numbers of the poling axis.

Moreover some parts within a wafer showed considerably different  $\epsilon_{33}^T$  although they had almost the same  $T_c$  in this study. This variation of the  $\epsilon_{33}^T$  within the wafer cannot be explained only by the effect of the composition variations. The quality of the crystal may make an effect on the low  $\epsilon_{33}^T$ . However, the PZNT 91/9 shows the rhombohedral and tetragonal phases at room temperature because the MPB composition is stable for both phases as above mentioned. Therefore the ratio of the phases may be considerably different at a certain part within a wafer. Moreover, Tsurumi et al. reported that two types of domain structure were observed within a (001) wafer of the PZNT 91/9 PSC and their electric properties were different from each other. [10] Regarding the possible causes of the characteristics variations within a wafer, not only the composition variations but also the crystal phases and domain structures should be considered. Therefore the relationship of characteristics variations with crystal phases and domain structures needs to be investigated.

#### 4. CONCLUSION

Variations of dielectric and piezoelectric properties,  $T_c$ ,  $\epsilon_{33}^T$ ,  $kt$ , between wafers and within a wafer of PZNT PSC were investigated. The following results were obtained:

- 1)  $T_c$  showed large variations between wafers. The average of the  $T_c$  at the end part is about 13°C lower than that at the initial part of the crystal.
- 2)  $T_c$  showed large variations within a wafer. The variation reduced gradually from the initial part to the end part of the crystal.
- 3)  $\epsilon_{33}^T$  showed large variations between wafers. The average of the  $\epsilon_{33}^T$  at the end part is about 1800 higher than that at the initial part of the crystal.
- 4)  $\epsilon_{33}^T$  showed large variations within a wafer. The variation reduced gradually from the initial part to the end part of the crystal.
- 5) The  $kt$  showed small variations between wafers and within a wafer of the crystal.

The coupling factor  $k_{33} > 80\%$ , dielectric constant after poling  $\epsilon_{33}^T > 3,000$  and piezoelectric constant  $d_{33} > 2,000$  pC/N of these novel PSC are quite attractive for piezoelectric devices in various fields. However, the present-day PZNT PSC has large characteristics variations. Characteristics variations between wafers may be mainly attributable to variations in composition. Obtaining highly homogeneous PZNT PSC by optimizing growth process is important for improving the characteristics variations. On the other hand, characteristics variations within a wafer should be considered not only variations in composition but also influences of the crystal phase, domain structure and defect chemistry. Once these problems are overcome, there is a strong possibility that PSC may become predominant for sophisticated, performance-oriented piezoelectric devices.

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